Influence of Oxygen Fugacity on the Solubility of Carbon and Hydrogen in FeO−Na₂O−SiO₂−Al₂O₃ Melts in Equilibrium with Liquid Iron at 1.5 GPa and 1400°C

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Abstract—Equilibria in the model melt $(NaAlSi_3O_8(80) + FeO(20))−C−H_2$ system were experimentally studied at $\Delta\log fO_2(IW)$ from −2.2 to −5.6, a pressure of 1.5 GPa, and a temperature of 1400°C. The experiments were conducted in a piston−cylinder apparatus using Pt capsules. The low fO_2 values were imposed during the experiments by adding 2, 5, and 7 wt % of finely dispersed SiC to $NaAlSi_3O_8(80) + FeO(20)$ powder. The experimental products were investigated by electron microprobe analysis and Raman spectroscopy. The investigations showed that melting at 1.5 GPa and 1400°C in the stability field of a metallic iron phase produces silicate liquids containing both oxidized and reduced H and C species. Carbon and hydrogen are dissolved in the melt as C−H (CH_4) complexes. In addition, OH⁻ groups, molecular hydrogen H_2, and molecular water H_2O were observed in the melts. The proportions of dissolved C and H species strongly depend on oxygen fugacity. With decreasing fO_2, the content of O−H species decreases and that of H−C species increases. The obtained data and previous results (Kadik et al., 2004, 2006) allow us to suppose a fundamental change in the character of magmatic transfer of C−O−H components during the evolution of the redox state of the Earth's mantle in geologic time toward higher fO_2 in its interiors.

PROBLEM FORMULATION

Interaction of volatile C−O−H compounds with the melting products of the early reduced mantle equilibrated with a metallic iron phase remains to be a poorly studied geochemical process. On the other hand, the knowledge of such chemical interactions is important for the understanding of the character of magmatic transport of volatile C−O−H compounds from the planetary interiors to the surface and estimation of their contribution to the formation of the early atmosphere. There is limited experimental evidence on the combined solubility of carbon and hydrogen in iron-bearing silicate melts [1, 2]. Investigations in the system iron-bearing melt (ferrobasalt)−Fe liquid phase−H_2−C [1, 2] conducted at 4 GPa and 1550–1600°C at low fO_2 values, which were selected on the basis of concepts on the initial redox state of mantle rocks within the chondrite and enstatite chondrite models of Earth formation [3, 4], showed that, despite the reduced conditions, hydrogen and carbon are dissolved at high pressures as both oxidized (OH⁻, H_2O, and CO_3^{2-}) and reduced species (H_2, CH_4, Si−C, and C). The relationships between them depend on fO_2.

This paper continues these studies and reports experiments on equilibria in the system model $(NaAlSi_3O_8 + FeO)$ melt−molten phase Fe−H_2−C at a pressure of 1.5 GPa, a temperature of 1400°C, and $\Delta\log fO_2(IW)$ from −2.2 to −5.6, where $\Delta\log fO_2(IW) = \log fO_2(IW) - \log fO_2^{exp}$ is the difference between the equilibrium oxygen fugacity of the Fe−FeO (IW) buffer and oxygen fugacity in the experiment. The goal of this investigation was to determine the character of combined hydrogen and carbon dissolution in this system at fO_2 values characteristic of the $T−P−fO_2$ conditions of the stability of the metallic phase and lower pressures compared with our previous studies [1, 2]. In addition to fO_2, pressure is another factor affecting the formation of C−O−H compounds in reduced magmatic melts, but the character of its influence remains poorly understood.

Table 1. Chemical compositions of starting mixtures, wt %

Run no.	System	SiO$_2$	Al$_2$O$_3$	Na$_2$O	FeO	Si	C	Total
10S	98%(Ab(80)+FeO(20))+2%SiC	53.66	15.51	9.23	19.60	1.40	0.60	100.00
11S	95%(Ab(80)+FeO(20))+5%SiC	52.02	15.03	8.94	19.00	3.50	1.50	99.99
12S	93%(Ab(80)+FeO(20))+7%SiC	50.93	14.72	8.76	18.60	4.90	2.10	100.01

Note: Ab is albite, NaAlSi$_3$O$_8$.

EXPERIMENTAL AND ANALYTICAL METHODS

The starting material of our experiments was a finely dispersed mixture of synthetic albite glass (NaAlSi$_3$O$_8$, 80 wt %) and ferrous oxide (FeO, 20 wt %).
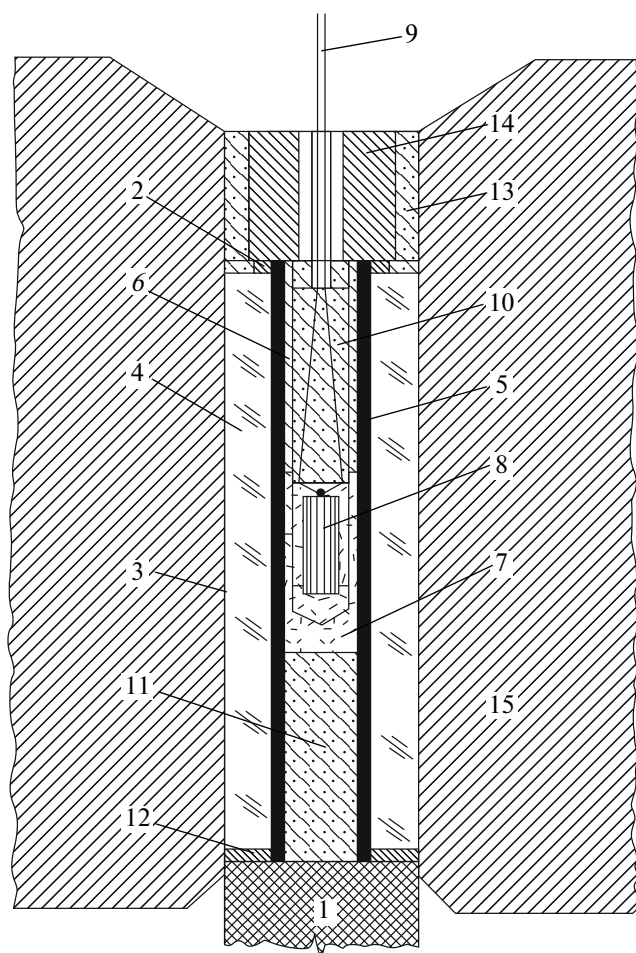

Fig. 1. Schematic cross-section of the cell assembly for the high-pressure piston–cylinder apparatus. (1) Piston, (2) upper conductor copper ring, (3) lead foil, (4) fluorite sleeve, (5) graphite heater, (6) upper pyrophyllite liner, (7) boron nitride insert, (8) sample in a capsule, (9) thermocouple, (10) small pyrophyllite spacer, (11) lower pyrophyllite spacer, (12) lower conductor copper ring, (13) isolating pyrophyllite rings, (14) electrode, and (15) pressure chamber.

Sodium aluminosilicate was selected for the experiments because of its low melting point and moderately hygroscopic properties. In order to maintain low fO_2 during the experiments, finely dispersed SiC was added to the mixture (2 wt % in experiment 10S, 5 wt % in experiment 11S, and 7 wt % in experiment 12S). The albite glass was prepared from the reagents SiO$_2$, Al$_2$O$_3$, and Na$_2$CO$_3$ preliminarily annealed for dehydration at temperatures of 1100 (SiO$_2$ and Al$_2$O$_3$) and 200°C (Na$_2$CO$_3$). The stoichiometric mixture of the oxides corresponding to the albite composition was finely ground in an agate mortar under ethanol for 3 h. Then the mixture was heated to 900°C for decarbonation at a rate of ~10°C/min in an alundum crucible in an Ar atmosphere at 1 atm and sintered at 900°C and 1 atm for 3–4 h. After air quenching, the decarbonated mixture was ground and remelted at 1400°C and 1 atm in an Ar flow in a graphite crucible for 3–4 h. The samples were quenched at a rate of ~100–200°C/s. At least three glass fragments were analyzed in order to check homogeneity. The synthetic albite glass was ground to a grain size of 20 μm. It was mixed in appropriate proportions with powdered SiC and FeO dried at 200°C for 24 h. The mixture of albite glass, FeO, and SiC was ground in an agate mortar under ethanol for 3 h, dried at 300°C for 6 h, and stored in a desiccator until its use in experiments. The chemical compositions of the starting mixtures are shown in Table 1.

Experiments were conducted in a piston–cylinder apparatus [5] at 1.5 GPa and 1400°C. The high-pressure cell assembly is shown in Fig. 1. Fluorite with low internal friction coefficient was used as a pressure-transmitting medium. Temperature was controlled using a Pt–Pt$_{10}$Rh thermocouple with an accuracy of ±10°C, and the uncertainty of pressure measurement was ±0.1 GPa. A sample approximately 200 mg in weight was loaded into a Pt capsule 5 mm in diameter, 15 mm high, and 0.2 mm wall thickness. A 0.2 mm thick graphite disk was placed below the sample. The sample was isolated from the walls of the Pt capsule with a 0.05 mm thick tungsten foil for the elimination of interaction between iron-bearing melt and Pt [6]. The experimental duration was 120 min. Experiments were quenched by shutting off power to the heater, and pressure was maintained constant during quenching in

order to prevent capsule rupture owing to decompression. The initial rate of quenching was ~200°C/s.

The method of hydrogen fugacity buffering used in the experiments was described in detail elsewhere [1, 2]. The fH_2 values in the cell assembly were imposed by reactions between traces of H_2O and the metallic units of the heater assembly at fO_2 values near the iron–wustite (Fe–FeO) buffer equilibrium (IW). Correspondingly, under given T, P, and fO_2, the fH_2O/fH_2 ratio of the O–H system outside the capsule is fixed. Within the Pt capsule, fO_2 is controlled by the reaction between the graphite disk, externally buffered H_2, and components of iron-bearing silicate melt. The latter is reduced with the release of O_2 and formation of a metallic iron phase via the reaction

$$2FeO = 2Fe + O_2. \qquad (1)$$
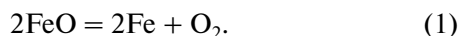
The starting SiC is unstable under the experimental conditions and is completely consumed in the reaction

$$SiC(init) + O_2 = SiO_2(melt) + C(graphite). \qquad (2)$$

The carbon produced in this reaction participates subsequently in reactions with the components of silicate melt and hydrogen. Equilibria (1) and (2) control fO_2 levels during the experiments.

The experimental values of fO_2^{exp} were expressed relative to the fO_2 of the Fe–FeO (IW) buffer equilibrium:

$$\Delta \log fO_2(IW) = \log fO_2(IW) - \log fO_2^{exp}, \qquad (3)$$

where $fO_2(IW)$ is the oxygen fugacity of the IW buffer equilibrium, and fO_2^{exp} is the oxygen fugacity in the experiment.

The fO_2^{exp} values were calculated on the basis of the empirical relation [7]

$$\log fO_2^{exp} = 2\log(X_{FeO}/a_{Fe}) - h/T(K) - \sum dX_i, \qquad (4)$$

which is based on experimental data for the equilibrium between the liquid iron phase and silicate melt in natural and model magmatic systems. In Eq. (4), h and d are the regression parameters, X_i are the components of silicate melts as oxides (mol %), $a_{Fe} = x_{Fe}\gamma_{Fe}$ is the activity of Fe in the metal alloy, x_{Fe} is the mole fraction of Fe, and γ_{Fe} is the activity coefficient of Fe. The γ_{Fe} values were taken to be 1 in our calculations. This assumption was based on the fact that γ_{Fe} is close to one in Fe–C alloys at high Fe mole fractions, which are 0.90–0.98 in our experiments. The $fO_2(IW)$ values were determined using the experimental data of [8].

The structure and chemical composition of glasses, Fe metal phase, and Pt were investigated by electron microprobe analysis. The speciation of C and H and mechanism of their simultaneous dissolution in the melt as a function of fO_2 were determined by Raman spectroscopy.

Electron microprobe analysis was carried out at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. Compositions were obtained using a CAMEBAX SX-100 (CAMECA) electron microprobe with four vertical spectrometers. Measurements were performed in two steps: major elements were determined first, after which carbon was analyzed by a special method. Carbon was analyzed using a PC2 pseudocrystal with an interplanar spacing of $2d = 97.46$ Å. In our case, there were no interferences of measured elements with carbon lines. Carbon was measured at an accelerating voltage of 10 kV, a beam current of 30 nA, and an electron beam diameter of 5 μm. During the development of the method of carbon analysis, we compared the results of analysis using carbon and aluminum coating. In the former case, a carbon-free material was mounted together with the analyzed sample in the same holder. Standards were pure carbon, tungsten carbide (WC) for the determination of carbon in the metal phase, and dolomite, $CaMgCO_3$, for the determination of carbon in the silicate part. In order to improve the statistical parameters of carbon analysis, the counting time on the peak was increased to 30 s. The detection limit for carbon was ~0.5 wt %.

The investigation of C–H bearing glasses by Raman spectroscopy was performed at the Fiber Optics Research Center, Russian Academy of Sciences. Raman spectra were recorded in 180° backscattering geometry using a T-64000 Jobin Yvon triple spectrometer equipped with a CCD sensor cooled with liquid nitrogen. The excitation beam of an Ar$^+$ laser (Spectra Physics) with a wavelength of 514.5 nm (5145 Å) was focused on the sample surface using a microscope with a 50× objective lens to a 2 μm spot. The scattered light was collected with the same microscope. The uncertainty of the determination of band position was no higher than 1 cm^{-1}.

EXPERIMENTAL RESULTS

Experiments were conducted at 1.5 GPa, 1400°C, and $\Delta \log fO_2(IW)$ values of −2.2 (run 10S), −3.7 (run 11S), and −5.6 (run 12S). Experimental products were examined under a microscope in transmitted and reflected light. They are colorless (runs 10S and 12S) and pale green (run 11S) glasses containing Fe droplets less than 1−2 μm in size (Fig. 2). The spherical shape of the Fe phase indicates that it was a liquid during the experiments. Gas inclusions were not observed in the glasses during microscopic examination, which implies that the melt was not saturated with respect to hydrogen- and carbon-bearing volatile compounds.

A characteristic feature of the chemical composition of glasses is that their FeO content decreases with decreasing fO_2 from 20 wt %, which corresponds to the
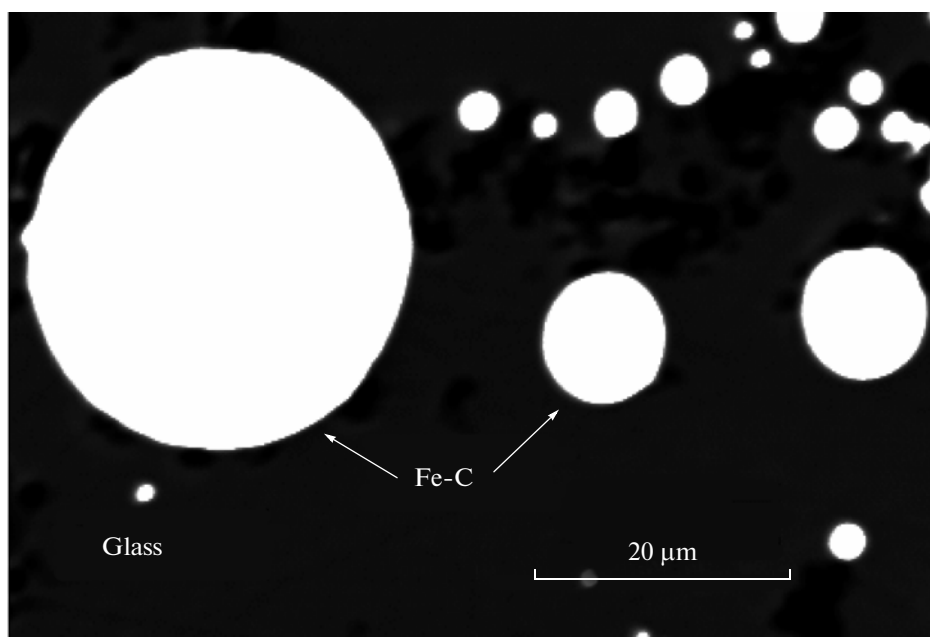
Fig. 2. Back-scattered electron image of the quenched products of experiment 11S (P = 1.5 GPa, T = 1400°C, and $\Delta\log fO_2$(IW) = −3.7) consisting of glass with droplets of metallic iron.

FeO content in the starting material, to 0.5 wt % at the lowest fO_2 (Table 2). This effect is due to FeO reduction in the melt with the formation of the liquid Fe phase via reaction (1).

According to reactions (1) and (2), the content of SiO_2 in the melt is controlled by two processes: the for-

mation of the Fe liquid phase with the removal of FeO from the melt and the oxidation of SiC in the starting mixture with the addition of certain amounts of SiO_2 to the melt, which is illustrated by Fig. 3. This diagram compares the SiO_2−FeO relationships in the experimental glasses with the contents of SiO_2 in the melt

Table 2. Chemical compositions of glasses and globules of a metallic phase produced in experiments at 1.5 GPa and 1400°C, wt %

			Glass			
Run	$\Delta\log fO_2$(IW)	SiO_2	Al_2O_3	Na_2O	FeO	Total
10S	−2.2	62.8	15.9	8.5	12.1	99.3
		(0.2)	(0.1)	(0.3)	(0.1)	
11S	−3.7	70.4	16.5	8.7	2.6	98.2
		(0.6)	(0.2)	(0.9)	(0.1)	
12S	−5.6	73.4	16.8	9.2	0.5	99.9
		(0.5)	(0.2)	(0.2)	(0.5)	

		Globules of a metallic phase			
Run	$\Delta\log fO_2$(IW)	Fe	Si	C	Total
10S	−2.2	95.8	0.1	2.8	98.7
		(0.1)	(0.0)	(0.2)	
11S	−3.7	96.2	0.1	4.0	100.3
		(0.3)	(0.0)	(0.7)	
12S	−5.6	96.3	0.4	3.6	100.3
		(0.4)	(0.0)	(0.4)	

calculated assuming that they were fully controlled by FeO reduction. Expectedly, the covariations of SiO_2–FeO and FeO in the experimental glasses indicate their enrichment in SiO_2 owing to the contribution of reaction (2) to the formation of the composition of the silicate liquid. In addition to optical examination, the chemical compositions of glasses suggest that SiC from the starting mixture was unstable under the experimental conditions and was completely consumed by reaction (2).

The contents of carbon in the glasses is <0.5, 3.4, and 4.1 wt % at $\Delta\log fO_2(\text{IW})$ of −2.2, −3.7, and −5.6, respectively.

The analyzed Fe metal globules (Table 2) contain 3−4 wt % of carbon, which is consistent with the known compositions of carbon-bearing iron alloys saturated with respect to carbon.

The Raman spectra of the glasses within the range 2500−4500 cm⁻¹ showed a number of bands, which can be assigned to the O−H, H−H, and C−H bonds in glasses.

O−H bonds. The Raman spectra of glasses in the high-frequency range (3000−3800 cm⁻¹) display a wide asymmetrical band at 3000−3700 cm⁻¹ with a maximum at 3567−3583 cm⁻¹ (Fig. 4). The shape of this band is similar to that observed in hydrous glasses [9] and hydrogen-bearing glasses in the Na_2O–Al_2O_3–SiO_2 system [10]. This band corresponds to the vibration of O−H bonds in H_2O molecules or OH^- groups in the structure of silicate melts. The intensity of this band decreases with decreasing fO_2.

H−H bonds. There is a weak band at 4124 cm⁻¹ at $\Delta\log fO_2(\text{IW})$ of −2.2, −3.7, and −5.6, which is assigned to molecular H_2 dissolved in glass [10].

C−H bonds. The Raman spectroscopy of glasses in the region of C−H bond vibrations reveals bands at 2909 cm⁻¹ and 3287−3291 cm⁻¹. According to [11], they correspond to the vibrations of molecular CH_4 or other hydrocarbon groups, such as CH_3^- or CH_2^{2-}.

Thus, our investigations indicate that the interaction of hydrogen and carbon with reduced silicate melts produces both reduced (H_2 and CH_4) and oxidized (OH^- and H_2O) species. The relationships between them are significantly dependent on fO_2. The main hydrogen compounds in the melts formed at $\Delta\log fO_2(\text{IW})$ from −2.2 to −3.7 are OH^- groups and H_2O. Part of hydrogen is dissolved in the molecular form. Carbon is dissolved as compounds with C−H bonds (CH_4). Under these conditions, the solubility of hydrogen is significantly higher than that of carbon. At a lower $\Delta\log fO_2(\text{IW})$ value of −5.6, the solubility of hydrogen as OH^- and H_2O is insignificant, whereas the solubility of carbon as C−H compounds (CH_4)
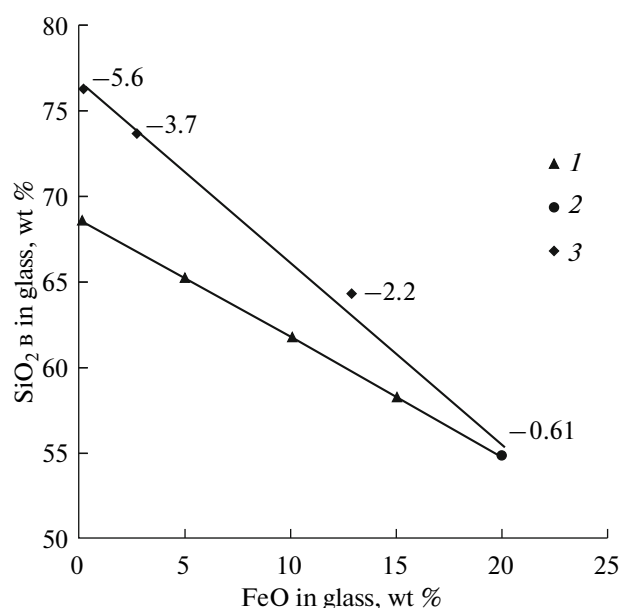

Fig. 3. Variations in SiO_2 in glasses as a function of FeO content: (*1*) calculated SiO_2 content determined on the basis of FeO reduction only, (*2*) contents of SiO_2 and FeO in the starting mixture $NaAlSi_3O_8$(80 wt %) + FeO (20 wt %) at $\Delta\log fO_2(\text{IW}) = -0.61$ correspond to the equilibrium of the molten starting mixture with an iron metallic phase at 1.5 GPa and 1400°C, and (*3*) contents of SiO_2 and FeO in glasses corresponding to fO_2 values during the experiments: $\Delta\log fO_2(\text{IW}) = -2.2$ in run 10S, $\Delta\log fO_2(\text{IW}) = -3.7$ in run 11S, and $\Delta\log fO_2(\text{IW}) = -5.6$ in run 12S.

increases, i.e., the mechanism of dissolution changes with decreasing fO_2.

The speciation of hydrogen and carbon in the model iron-bearing melt of the FeO–Na_2O–SiO_2–Al_2O_3 system at 1.5 GPa is identical to that detected previously [1, 2] in ferrobasalt melts and melts of the FeO–Na_2O–SiO_2–Al_2O_3 system at a pressure of 4 GPa. In both cases, the Raman spectra of the glasses indicate that reduced (H_2 and CH_4) and oxidized (OH^- and H_2O) species of hydrogen and carbon are formed in the melts. It can be concluded that a pressure decrease from 4 to 1.5 GPa at constant fO_2 did not affect the speciation of dissolved volatile compounds of carbon, hydrogen, and oxygen in silicate melts in equilibrium with carbon-bearing iron melt.

SOLUBILITY OF C−O−H COMPLEXES IN THE REDUCED MELTS OF THE EARTH'S EARLY MANTLE

The degassing of accreted material owing to impact processes, extensive heating, and melting of deep matter with the formation of the magma ocean is considered to be the main reason for the transportation of
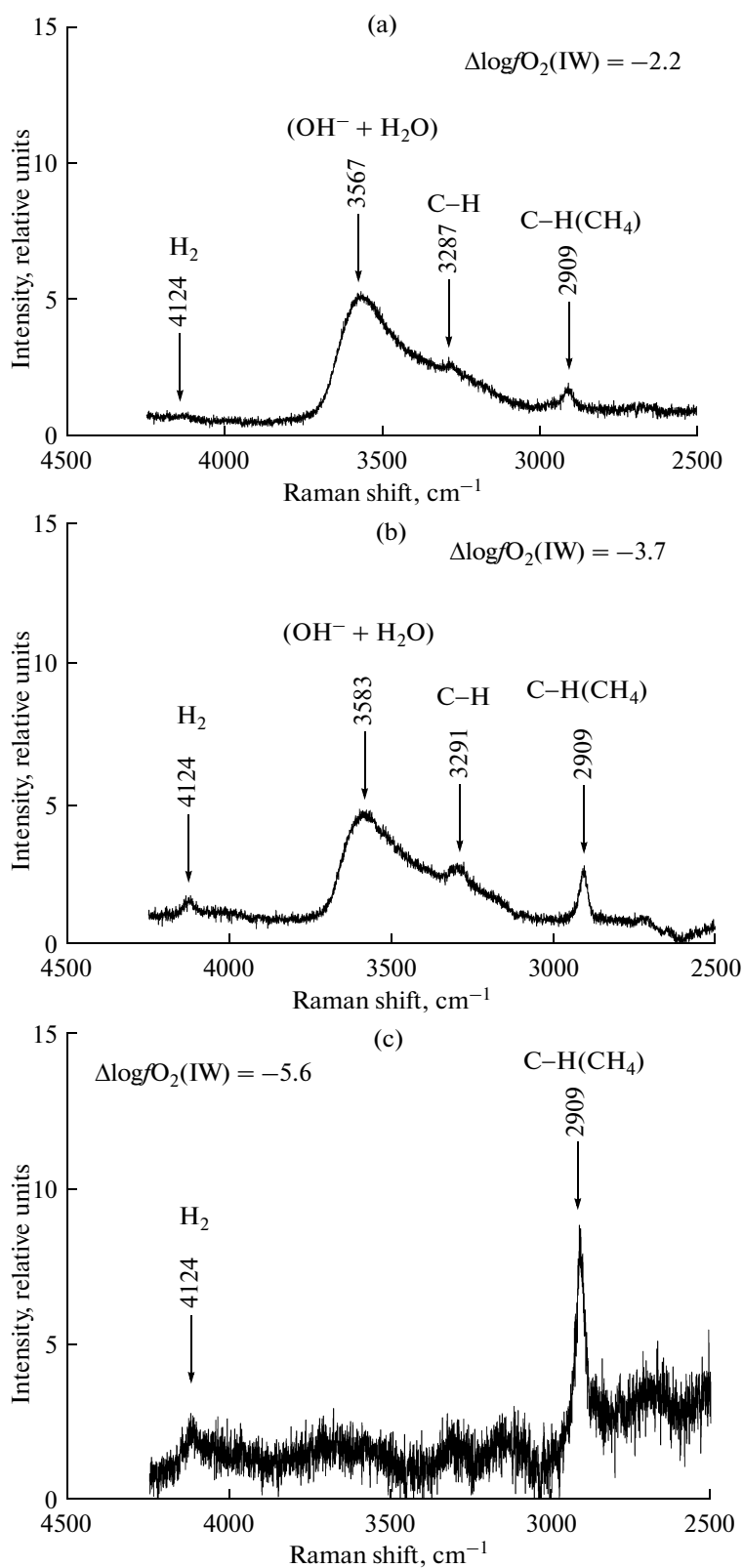
Fig. 4. Raman spectra of H−C-bearing glasses from experiments at $P = 1.5$ GPa and $T = 1400°C$: (a) run 10S, $\Delta \log f O_2(IW) = -2.2$; (b) run 11S, $\Delta \log f O_2 (IW) = -3.7$; and (c) run 12S, $\Delta \log f O_2 (IW) = -5.6$.

volatile components in the planetary interiors and the formation of the Earth's early atmosphere [12, 13]. The proportions of reduced (CH_4, H_2, and CO) and oxidized (H_2O and CO_2) hydrogen and carbon compounds introduced into the upper levels of the Earth owing to early volcanic activity are still disputable. Meanwhile, the elucidation of the characteristics of the magmatic transport of planetary volatile components during metal phase segregation in the Earth and metallic core evolution is extremely important for establishing the source of gaseous carbon, hydrogen, and nitrogen compounds, which are believed to contribute to the formation of the early reduced atmosphere of our planet. It was suggested that high CH_4 concentrations in it were essential for the prebiological evolution of organic matter, which resulted in the origin of life on the surface of the Earth [14].

The investigations reported here and previous results [1, 2] allow us to consider the evolution of the redox conditions of the Earth's early mantle as an important factor affecting the character of the magmatic transport of C−O−H components through geologic time.

It is thought that the primary reason for the evolution of fO_2 in the upper part of the mantle through geologic time is the multistage character of the formation of the Earth's metallic core [15]. After the formation of the major portion of the core (~95%) during the earliest 100 million years of Earth evolution, its growth continued slowly, but already owing to the disproportionation reaction of FeO in the mantle:

$$3Fe^{2+}O(mantle) \longrightarrow Fe^0 (core) + Fe_2^{3+}O_3(mantle).$$
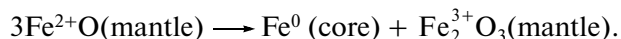
The second stage had lasted for subsequent 150–300 million years and resulted in an increase in the chemical potential of oxygen in the upper parts of the mantle owing to phase transformations during the ascent of mantle materials.

The first stage of core growth occurred under the conditions of the existence of the reduced primordial matter of the Earth and was accompanied by intense volcanic activity and formation of volcanic gases dominated by CH_4, H_2, and CO. During the second stage, the dominant volatile compounds of carbon and hydrogen became H_2O and CO_2, i.e., the most abundant volatile components of modern magmatism.

CONCLUSIONS

(1) The investigation of the influence of oxygen fugacity on the solubility of carbon and hydrogen in $FeO–Na_2O–SiO_2–Al_2O_3$ melts in equilibrium with liquid iron at 1.5 GPa and 1400°C suggests that reduced (H_2 and CH_4) and oxidized (OH^- and H_2O) hydrogen and carbon species are formed in them.

(2) The solubilities of hydrogen and carbon and the mechanism of their dissolution are strongly dependent on fO_2. At $\Delta\log fO_2$(IW) values of −2.2 and −3.7, hydrogen is dissolved in the melt mainly as oxidized species (OH^- and H_2O), and carbon is dissolved as compounds with C−H bonds. At a lower $\Delta\log fO_2$(IW) of −5.6, the mechanism of dissolution is different: the contribution of OH^- and H_2O to the solubility of hydrogen is insignificant, whereas the solubility of carbon in the from of compounds with C−H-type bonds (CH_4) increases.

(3) The obtained characteristics of hydrogen and carbon dissolution in the model iron-bearing melt of the $FeO–Na_2O–SiO_2–Al_2O_3$ system at 1.5 GPa are identical to those detected previously for ferrobasalt melts and melts of the $FeO–Na_2O–SiO_2–Al_2O_3$ system at a pressure of 4 GPa [1, 2]. Hence, it can be concluded that a pressure decrease from 4 to 1.5 GPa at constant fO_2 does not affect the speciation of volatile compounds of carbon, hydrogen, and oxygen in silicate melts in equilibrium with liquid iron.

(4) The investigations reported here and the results of previous studies [1, 2] allowed us to suppose a dramatic change in the character of the magmatic transfer of C−O−H components during the evolution of the redox state of the Earth's mantle through geologic time toward an increase in fO_2 in its interiors.

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